PROGRESS IN ANALYTICAL SPECTROSCOPY

Volume 11

Editor-in-Chief

C. L. CHAKRABARTI

Carleton University, Ottawa, Canada

Executive Editor

R. E. STURGEON

National Research Council of Canada, Ottawa, Canada

Editors

J.-M. MERMET

Université Claude Bernard, Lyon, France

E. S. YEUNG

Iowa State University, Ames, Iowa, U.S.A.

M. W. BLADES

University of British Columbia, Vancouver, Canada

N. J. DOVICHI

University of Alberta, Edmonton, Canada

PERGAMON PRESS

OXFORD · NEW YORK · BEIJING · FRANKFURT · SÃO PAULO · SYDNEY · TOKYO · TORONTO

Progress in Analytical Spectroscopy

Editor-in-Chief

C. L. Chakrabarti, *Department of Chemistry, Carleton University, Ottawa, Ontario, Canada K1S 5B6*

Executive Editor

R. E. Sturgeon, *Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6*

Editors

J.-M. Mermet, *Laboratoire des Sciences Analytiques, Université Claude Bernard, Lyon, 69622 Villeurbanne Cedex, France*
E. S. Yeung, *Department of Chemistry, Iowa State University, Ames, IA 50011, USA*
M. W. Blades, *Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6*
N. J. Dovichi, *Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2*

Editorial Advisory Board

Chairman: **Professor J.D. Winefordner,** Department of Chemistry, University of Florida, USA
R.M. Barnes, University of Massachusetts, USA
Huang Benli, Xiamen University, Xiamen Fujian, PRC
S.S. Berman, National Research Council of Canada, Ottawa, Canada
J.E. Bertie, Department of Chemistry, University of Alberta, Canada
P.W.J.M. Boumans, Phillips Research Laboratories, Eindhoven, The Netherlands
L.R.P. Butler, Groen Kloof, South Africa
L. de Galan, Unilever Research Laboratory, Vlaardingen, The Netherlands
K. Dittrich, Karl-Marx Universität, Leipzig, DDR
H. Falk, Akademie der Wissenschaften der DDR, Berlin, DDR
W. Frech, University of Umea, Sweden
K. Fuwa, National Institute for Environmental Studies, Japan
A.L. Gray, University of Surrey, UK
P. Griffiths, University of California, Riverside, USA
T.D. Harris, AT & T Bell Laboratories, NJ, USA
G.M. Hieftje, Indiana University, Indiana, USA
J.A. Holcombe, University of Texas at Austin, USA
G. Horlick, Department of Chemistry, University of Alberta, Canada
A. Hulanicki, University of Warsaw, Poland
Li Jiaxi, Institute of Rock and Mineral Analysis, Beijing, PRC
R.A. Keller, Los Alamos National Laboratory, NM, USA
S.F.A. Kettle, University of East Anglia, UK
B.V. L'vov, Polytechnical Institute, Leningrad, USSR
J.P. Matoušek, University of New South Wales, Australia
M. Morris, University of Michigan, USA
T. Nakahara, University of Osaka Prefecture, Japan
T.C. O'Haver, University of Maryland, MA, USA
N. Omenetto, Ispra Establishment, Ispra (Varese), Italy
A. Petrakiev, Sofia University, Bulgaria
E.H. Piepmeier, Oregon State University, USA
T.C. Rains, National Bureau of Standards, Washington D.C., USA
J.M. Ramsay, Oak Ridge National Laboratory, TN, USA
C.N.R. Rao, Indian Institute of Science, Bangalore, India
J. Robin, Institut National des Sciences Appliquées de Lyon, France
I. Rubeska, Geological Survey of Czechoslovakia, Prague, Czechoslovakia
W. Slavin, The Perkin-Elmer Corporation, Norwalk, Connecticut, USA
J. Steinfeld, Massachusetts Institute of Technology, USA
V. Sychra, Prague Institute of Chemical Technology, Czechoslovakia
G. Tessari, Istituto di Chimica Analitica, Universita di Bari, Italy
G. Tolg, Institut für Spektrochemie, Dortmund, FRG
E. Wehry, University of Tennessee, USA
B. Welz, The Perkin-Elmer Corporation, Uberlingen, FRG
Ni Zhe-ming, Academy of Sciences, Beijing, PRC
K. Zimmer, Lorind Eötvös University, Budapest, Hungary

Progress in Analytical Spectroscopy is published as one volume of six parts per year.
1989 Subscription rate: DM 495.00 (including postage and insurance). Two year subscription (1989/90): DM 940.50
Specially Reduced Rates to Individuals: Any individual whose institution takes out a library subscription may purchase a second or additional subscription for personal use at a much reduced rate of DM 143.00 per annum.
Prices are subject to change without notice.
Subscription enquiries from customers in North America should be sent to Pergamon Press Inc., Maxwell House, Fairview Park, Elmsford, NY 10523, U.S.A., ***and for the remainder of the world to*** Pergamon Press plc., Headington Hill Hall, Oxford OX3 0BW, U.K.

Copyright © 1989 Pergamon Press plc.

It is a condition of publication that manuscripts submitted to this journal have not been published and will not be simultaneously submitted or published elsewhere. By submitting a manuscript, the authors agree that the copyright for their article is transferred to the publisher if and when the article is accepted for publication. However, assignment of copyright is not required from authors who work for organizations which do not permit such assignment. The copyright covers the exclusive rights to reproduce and distribute the article, including reprints, photographic reproductions, microform or any other reproductions of similar nature and translations. No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, electrostatic, magnetic tape, mechanical, photocopying, recording or otherwise, without permission in writing from the copyright holder.

Photocopying Information for Users in the USA. The Item-Fee Code for this publication indicates that authorization to photocopy items for internal or personal use is granted by the copyright holder for libraries and other users registered with the Copyright Clearance Center (CCC) Transactional Reporting Service provided the stated fee for copying, beyond that permitted by Section 107 or 108 of the United States Copyright Law, is paid. The appropriate remittance of $0.50 per page is paid directly to the Copyright Clearance Center Inc., 27 Congress Street, Salem, MA 01970.

Permission for other use. The copyright owner's consent does not extend to copying for general distribution, for promotion, for creating new works, or for resale. Specific written permission must be obtained from the publisher for such copying.

The Item-Fee Code for this publication is: 0884–1837/88 $0.00 + .50

Back issues of all previously published volumes are available direct from Pergamon Press. Back issues of Pergamon journals in microform can be obtained from UMI, 300 North Zeeb Road, Ann Arbor, MI 48106, U.S.A.

Publishing/Advertising Offices

Pergamon Press plc., Headington Hill Hall, Oxford OX3 0BW, England
Pergamon Press Inc., Maxwell House, Fairview Park, Elmsford, New York 10523, USA

CONTENTS

Photoacoustic Impulse Response Testing (PIRT) as a Method for the Non-Destructive Evaluation of the Spectral and Spatial Depth-Profiles of Solid Samples 1
I. P. VICKERY

Glow Discharge Mass Spectrometry 53
W. W. HARRISON and B. L. BENTZ

Surface Enhanced Raman Spectroscopy of Small Biological Molecules 111
R. F. PAISLEY and M. D. MORRIS

Electronic and Vibrational Spectroscopy of Electrochemical Events 141
R. L. MCCREERY

Thermo-Optical Spectroscopy for Trace Microchemical Analysis 179
N. J. DOVICHI

Regression Methods in Analytical Chemistry 209
J. D. HWANG and J. D. WINEFORDNER

Evaluation of Hydride Generation and Atomization for AAS 251
J. DĚDINA

Picosecond Spectroscopy in Analytical Chemistry 361
M. J. WIRTH

Fluorescence Lifetime Selectivity in Chemical Analysis 383
L. B. MCGOWN

Experimental and Theoretical Investigations Relating to FANES 417
H. FALK, E. HOFFMANN and CH. LÜDKE

Fiber Optic Affinity Sensors in Chemical Analysis 481
M. J. SEPANIAK, B. J. TROMBERG and T. VO-DINH

Determination of Trace Elements in Biological Fluids other than Blood by Graphite Furnace Atomic Absorption Spectrometry 511
K. S. SUBRAMANIAN

AUTHOR INDEX

Bentz, B. L. 53

Dědina, J. 251
Dovichi, N. J. 179

Falk, H. 417

Harrison, W. W. 53
Hoffman, E. 417
Hwang, J. D. 209

Lüdke, Ch. 417

McCreery, R. L. 141
McGown, L. B. 383
Morris, M. D. 111

Paisley, R. F. 111

Sepaniak, M. J. 481
Subramanian, K. S. 511

Tromberg, B. J. 481

Vickery, I. P. 1
Vo-Dinh, T. 481

Winefordner, J. D. 209
Wirth, M. J. 361

SUBJECT INDEX

AAS interference. *See* Hydride generation AAS; Hydrogen generation AAS
Aluminium, determination in urine 516–19
Amino acids, surface-enhanced Raman spectroscopy (SERS) 115–22
Amniotic fluid, determination of trace elements in 580
Analysis-of-variance (ANOVA) 216
Antimony, determination in urine 566
Arsenic, determination in urine 519–23
Atomic absorption coefficient 316–24
  at higher temperature 324
  at low temperature in hydrogen environment 323–4
Atomic absorption spectroscopy (AAS). *See* Hydride generation AAS; Hydrogen generation AAS

Beer's law 180, 181
Beryllium, determination in urine 566
Bile, determination of trace elements in 580
Bile pigments, surface-enhanced Raman spectroscopy (SERS) 136
Biological fluids
  determination of trace elements in 511–608
  see also under specific fluids
Biomedical Computer Program (BMDP) 218
Bismuth, determination in urine 576
Breath, determination of trace elements in 592

Cadmium, determination in urine 523–31
Catecholamines, surface-enhanced Raman spectroscopy (SERS) 132–3
Cathodic sputtering 61–3
  ionization modes 68–71
  plasma processes 66–8
  threshold energies 64
Cerebrospinal fluid (CSF), determination of trace elements in 592–3
Characteristic time constant 294, 297, 342
Chemometrics 209
Chromatographic detection 408
Chromium, determination in urine 531–9
Cobalt, determination in urine 539–42
Convolution theorem 13–15
Copper, determination in urine 576–7
Correlation 12–13
Crossed-beam interferometry 204
Crossed-beam photothermal deflection 203
Crossed-beam thermal lens 194–203
  determinations in neat solutions 197
  liquid chromatography detection 198–9
  photothermal microscope 200–3
  theoretical studies 194–6
Crossed-beam thermo-optical methods 182–93

Diffusion coefficients 314–16

Eigenvalues 214
Eigenvectors 214
Electrochemical events 141–77
Electrochemistry, and spectroscopy 142–6
Electronic spectroscopy 141–77
Extra-cavity pulse compression 366

FANES 417–80
  analyte production rate in sputtering systems 455
  analytical applications 463–76
  analytical signal 446–9
  applications of 473–6
  assessment of 476–8
  atomic vaporization 451–2
  atomization efficiency of AES sources 453–60
  background emission 460–3
  comparison of efficiency of atomizers 455–7
  current-voltage characteristics 423–5
  density of neutral particles 444–6
  detection limits 463, 470–1
  detection sensitivity 422
  determination of Ag in Au 464–5
  determination of doped elements in deionized water 466–7
  determination of doped elements in HNO_3 468–73
  determination of Na in Al 464–5
  discharge formation 422
  dynamic range 463–4
  electron density 443
  emission intensity of analyte material 432
  emission of spectra 426–33
  figures of merit 463–4
  hollow cathode discharge (HCD) effect 421
  influence of nonthermal plasma on degree of dissociation 457–60
  instrument description 420–1
  instrumental requirements 476–7
  intensity of discharge gas lines 428–30
  intensity of sputtered material 430–2
  molecular vaporization 451–2
  mono-element determination with internal standard 464–5
  multi-element determination 465–73
  organic matrices 473
  particle densities 443
  plasma temperature 433–41
  possibilities for advancing 478
  reproducibility 463, 470–1
  selection of lines and elements 439–40
  solid plant substances 474–6
  temperature measurement 440–1

vaporization of samples 446–52
vaporization temperature 449–51
Fast photomultipliers 373
Feedback shift register 15
Fiber optic affinity sensors 481–509
applications 495–506
competitive-binding 499–500
competitive-equilibrium-binding 502
direct assay 500–1
distal face sensors 487–8
enzyme-based 503–4
enzyme-measuring 504–5
fluorescence collection efficiency 488–92
fluoroimmunoassay (FIA) techniques 495, 497–8
immunochemical-based 495–503
instrumentation 486–95
light coupling 486–7
optical background levels 488–92
response kinetics for competitive-equilibrium-binding sensors 503
sensing termini 492–5
total internal reflection fluorescence (TIRF) 492, 499
Fiber optics, principles of 482–6
Flame atomic absorption spectroscopy (FAAS) 419
Flavins
surface-enhanced Raman spectroscopy (SERS) 135–6
surface-enhanced resonance-enhanced Raman scattering (SERRS) 135–6
Fluorescence lifetime selectivity 383–415
analysis of complex samples 399–404
and fluorescence spectra 389–91
chromatographic detection 408
immunochemical methods 404–5
instrumentation 389
interferences 397–9
quantitative analysis 391–7
quantitative determinations 394–7
theory 385–9
Fluorescence lifetime studies 375
Frequency domain spectroscopy 369–70
Frequency domain techniques 373–5
Furnace Atomic Nonthermal Excitation Spectroscopy. *See* FANES

Gallium, determination in urine 577
Gas discharge
characteristics of 56
theory 56
Gauss–Newton procedure 226–8
Glow discharge
analytical potential 55
as spectroscopic source 54
cathodic sputtering 61–3
dc 57, 71, 76
Grimm design 72
hollow cathode 60–1, 72–4
hollow cathode plume (HCP) ion source 74
ion sources 71–6
operative principles 56
power requirements 76
pulsed 76
reviews 55
rf 60
sputtered neutral high frequency sources 74–5
sputtering rate 63
sputtering yield 63
Glow discharge mass spectrometry (GDMS) 53–110
analysis procedure 84–6
analytical considerations 83–8
applications 89–103
bulk metals analysis 89–94
commercially available instruments 80–3
compacted materials 94–7
instrumentation 77, 79–80
interferences 87–8
negative ions 102–3
plasma processes 101–2
potential of 104
problems of 104
quadrupole based spectrometer 78
reviews 55
sample preparation 83–4
sampling 77–8
semiconductors 100
sensitivity 87
solutions 99
sputter gases 63
standards 86–7
thin films 97–8
Gold, determination in urine 542–6
Graphite furnace atomic absorption spectroscopy (GFAAS) 419, 511–608
Graphite furnaces 264, 286

Herbicides, action on leaves 34
Heterogeneity analysis 393
High precision absorbance determination 181
Hip-joint fluid, determination of trace elements in 593
Hollow cathode discharge (HCD) 419
Homoskedasticity 224
Hydride atomization
analyte transfer in atomizer bar-tube 274–6
dependence of absorbance on free atom distribution in bar-tube 310
diffuse flames 263
externally heated quartz tubes 276–81
flame-in-tube atomizers 268–76
graphite furnaces 264–8
in-situ trapping 264–5
laminar flow model 304, 309–10, 330
mathematical description of 292–311
mechanisms of 271–3
methods of 263–81
on-line atomization 264, 266–7
plug flow model 304, 306–9, 330
well-stirred tank model 304–6, 308–9, 330
see also Selenium hydride atomization

Hydride forming elements 257
Hydride generation 257
  batch mode 262, 287, 289
  cold trap collection 263
    with closed system heating 263
  collection mode 262
  continuous flow mode 262
  direct transfer mode 262
  efficiency 260–1, 289
  flow injection mode 262
  in-situ trapping 262
  methods of 262–3
  pressure collection 263
  trace analysis 348–52
  use of term 259
Hydride generation AAS, interferences 282–92
Hydride release 260–1, 292, 293, 303, 350
  efficiency 259–61, 295, 302, 340
  use of term 259
Hydride supply function 292, 294, 296, 298–303, 309, 312, 325, 326, 340, 342, 345
Hydride transport 261
  efficiency 259, 296, 300, 303, 333, 335–6, 350
Hydrogen generation
  accuracy 353
  batch mode 298–301
  cold trap collection 302–3
  continuous flow mode 294–6
  dependence of free atom distribution in bar-tube of flame-in-tube atomizer 303–10
  diffuse flames 286
  externally heated quartz tubes 290–2
  flame-in-tube atomizers 287
  flow injection mode 296–8
  general assessment of methods 353–4
  graphite furnaces 286
  in-situ trapping 286
  mathematical description of 292–311
  microanalysis 347–8
  on-line atomization 286
  open system heating 303
  pressure collection 301–2
  sensitivity 347–54
  theoretical models 293
  trace analysis 348–54
  see also Selenium hydride generation
Hydrogen generation AAS
  analyte decay interference 287–8, 290, 292
  compound interferences 284
  gaseous phase interferences 282
  interferences in atomizer 286–92
  liquid phase interferences 282–5
  matrix interferences 284–5
  memory analyte decay interferences 290
  nonspectral interferences 282
  radical population interferences 287, 288, 290, 292
  release efficiency interference 288
  release kinetics interference 283
  transport efficiency interferences 288
  transport interferences 285–6
  transport kinetics interference 283, 288
Immunochemical methods 404–5
Impulse response testing 17
Inductively coupled plasma (ICP) 419
Infrared reflectance/absorbance techniques 171–4
Integral atomization efficiency 264, 274
Intra-ocular fluid, determination of trace elements in 593
Inverse least squares method 225
Iron, determination in urine 577

Lambert–Beer law 310, 316
Lead, determination in urine 546–53
Leaves
  acid damaged 39–42
  herbicidal action 34
  mould-infected 45–7
  photoacoustic properties 28
  PIRT imaging 39
  rust-infected 42
Linear systems, evaluation of 12–16
Linearization method 226–8
Local atomization efficiency 264, 273, 287, 303, 312

Manganese, determination in urine 553
Maximal-length shift register sequences 15–16
Mercury, determination in urine 577
Microchemical analysis 179–207
Mode-beats 370–1
Mode-locked pulses, time and frequency domain properties 369–71
Mode-locking
  acousto-optic 364–5
  experimental methods 364–6
  passive 365–6
  theory 362–4
Multicollinear chemical data 237–42
Multiple coefficient of determination 215
Multiple linear regression (MLR) 223

NAD/NADH, enzyme-based FOAS employing 505–6
Nickel, determination in urine 556

Optical fibers. *See* Fiber optics
Ordinary least squares (OLS) method 214

Palladium, determination in urine 542–6
Penicillin, enzyme-based FOAS 505
Peptides, surface-enhanced Raman spectroscopy (SERS) 115–22
Perspiration, determination of trace elements in 595
Phase-modulation techniques 389, 393, 408
Phase-resolved determinations 393
Phase-resolved excitation-emission matrices (PREEMs) 389, 401

Phase-resolved flourescence spectroscopy 401
Phase-resolved techniques 397, 405, 408
Photoacoustic detection
  gas microphone cell 8–9
  piezoelectric 8–9
Photoacoustic effect 5
  measurement of 6
  theory 6
Photoacoustic imaging 37–47
  applications 38
  image detection 37–8
Photoacoustic impulse response testing (PIRT) 1–52
  further applications 33–4
  herbicidal action 34
  history 17–36
  imaging 39
  leaves 28–32
  polymer samples 22–7
  pulse and PRBS methods 18
  single frequency depth-profiling 21
  single impulse response comparisons 28–9
  single wavelength 18–20
  spectroscopic 20–7, 30–2, 39
  time dependent phenomena 34–6
Photoacoustic spectroscopy 5
  biochemical analysis 10
  biological samples 9–11
  instrumentation 7, 21
  intact tissues 9–10
  lock-in amplification 9
  modulation system 8
  novel applications 10–11
  optical system 7
  radiation sources 7
Photothermal microscope 200–3
Picosecond laser pulses 361
Picosecond pulse generation and characterization 362
Picosecond spectroscopy 361–81
  applications 375–9
  experimental techniques 372–5
  optical timing methods 372–3
Piezoelectricity 8–9
Plant pigments, surface-enhanced Raman spectroscopy (SERS) 136
Platinum, determination in urine 542–6
Porphyrins, surface-enhanced resonance-enhanced Raman scattering (SERRS) 133–4
Pseudo-random binary sequence (PRBS) 15
Pulsed-excitation technique 389, 391–3
Purines, surface-enhanced Raman spectroscopy (SERS) 122–32
Pyrimidines, surface-enhanced Raman spectroscopy (SERS) 122–32

Quenching effects, elimination of 397–9

Raman emission, rejection of fluorescence from 375–7
Raman resonance scattering, bile pigments 136
Raman spectroelectrochemistry
  generalized cell configuration 163
  single wavelength 166–7
  solution components 162–8
Regression methods 209–49
  all possible 230–2
  best subset selection method 232–3
  biased 237–42
  computer programs and packages 218–19
  flowchart 210
  for analysis and interpretation of chemical data 220–5
  fundamental principles of 213–19
  general linear 221
  nonlinear 226–8
  overall objectives of 210
  principal component 240–2
  ridge regression 239–40
  stepwise 233–6
  variable selection 229–36
Regression model
  linear 216
  physically or statistically significant 219
  precision of 215
Rotational diffusion measurements 377–9

Saliva, determination of trace elements in 593–4
Selenium, determination in urine 560–2
Selenium hydride atomization 312–32
  analyte transfer in flame-in-tube atomizers 312
  atomic absorption coefficient 316–24
    at higher temperature 324
    at low temperature in hydrogen environment 323–4
  atomizer bar-tube parameters 313–14
  diffusion coefficient 314–16
  flame-in-tube atomizer 323
  generator outlet functions 312–13
  laminar flow model 328, 329, 331
  optimization of atomizer dimensions 331–2
  plug flow model 328, 331, 332
  well-stirred tank model 328
Selenium hydride generation
  batch generation 342–5
  batch mode 335
  cold trap collection
    methods of 336–9
    with closed system heating 336–8
    with open system heating 335, 338–9
  continuous flow 335, 339–41
  evaluation of method 332–46
  k_2/k_1 ratio 333–5
Semen, determination of trace elements in 594–5
Short path length samples 180–1
Short pulse characterization 366–9
Short pulse generation and detection 362–9
Silicon, determination in urine 578
Silver, determination in urine 578
Simple linear regression (SLR) 221

Spectroelectrochemistry, electrode surface 170–3
Spectroscopy, and electrochemistry 142–6
Spline (or segmented-curve) regression analysis 225–6
Statistical analysis system (SAS) 218
Statistical Package for the Social Sciences (SPSS) 218
Steenbeck minimum principle 421
Surface-enhanced Raman spectroscopy (SERS) 111–40
  amino acids 115–22
  bile pigments 136
  catecholamines 132–3
  flavins 135–6
  peptides 115–22
  purines 122–32
  pyrimidines 122–32
  techniques 114–15
Surface-enhanced resonance-enhanced Raman scattering (SERRS) 112
  flavins 135–6
  porphyrins 133–4
Surface enhancement, phenomena and theories 111–14
Surface infrared absorption spectroelectrochemistry 170–3
Surface Raman spectroscopy 170–1
Sweat, determination of trace elements in 595
Synchronous pumping 366
Synovial fluid, determination of trace elements in 595–6

Thallium, determination in urine 578
Thermal grating 204
Thermodynamic binding parameters 399
Thermo-optical spectroscopy 179–207
  alternative crossed-beam techniques 205
  optical propagation 187–92
  phase shift 187–8
  refractive index profile 186
  temperature rise 182–6
  theory 182
  thermal deflection 188–90
  thermal lens focal length 191–2
  trace microchemical absorbance determination 182–93
  see also Crossed-beam thermal lens
Time domain spectroscopy 369
Time-resolved fluorescence spectroscopy 361
Time-resolved techniques 397, 405, 408
Tin, determination in urine 579
Total gas flow 292, 294, 296, 303, 312
Trace elements
  determination in biological fluids 511–608
  determination in urine 516–79
  see also under specific elements
Transient spectroelectrochemistry 148
Transmission measurements, limitations of 180–1

Urine, determination of trace elements in 516–79
UV-visible absorption spectroelectrochemistry 146–50
  electrochemical diffusion layer 159
  general diffraction geometry 156–8
  parallel absorption methods 151
  parallel geometry 150–8, 161
  refractive index methods 152
  spatially resolved parallel absorption 154

Vanadium, determination in urine 562
Variable selection methods 229–36
Vibrational spectroscopy 141–77

Weighted linear regression (WLR) 224–5